The Anode Layer in the Electrolytic Polishing of Copper[1]

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ABSTRACT

The viscosities and electrical conductivities of solutions of $CuHPO_4$ in aqueous phosphoric acid and phosphoric acid-glycerol-ethylene glycol mixtures were measured with a view to investigating the anode layer formed when copper is electrolytically polished in these solutions. Dissolved copper was found to raise the viscosity considerably, the increase being greater in the mixtures with glycol and glycerol than in phosphoric acid alone. The copper concentration near the anode during electrolysis was measured, and current-voltage relationships were studied using a rotating copper anode. The effective thickness of the anode layer was estimated to be about 10^{-3} cm.

Introduction

Electrolytic polishing is the smoothing or brightening of a metal surface by anodic dissolution in an electrolytic cell. Normally, anodic dissolution of a metal makes the surface rougher, but if the electrolyte is suitably chosen and the right range of current densities and temperatures employed, the irregularities are smoothed out and a bright surface results. The amorphous layer characteristic of mechanical polishing is absent, and the surface is not flat, but slightly wavy; some people, therefore, prefer to call the process "brightening" rather than polishing. However, the name "electrolytic polishing" is in general use. A great many metals have been polished electrolytically, and the process has seen considerable commercial development in the last twenty years (4, 8, 12, 18).

The first systematic study of electrolytic polishing was made by Jacquet (10, 11). He showed that a surface of copper could be polished by making it the anode in a fairly concentrated aqueous solution of orthophosphoric or pyrophosphoric acid, provided the current density is not too low nor the temperature too high. During polishing a thin, viscous layer of solution, rich in copper salts, is seen to form on the anode surface. Jacquet reasoned that this obstructs the dissolution of the metal, either by its ohmic resistance or by hindering the diffusion of copper salts away from the surface. Where there are projections on the metal surface, this layer is relatively thin, and dissolution relatively fast. The result is a gradual leveling down of the surface as electrolysis proceeds.

This mechanism of electrolytic polishing of copper in phosphoric acid was affirmed by Elmore (7), who measured the rate of decrease of the anodic current with time as the viscous layer is built up. He regarded the process as essentially one of concentration polarization, in which the rate of dissolution of the copper is governed solely by the diffusion of cupric salts away from the anode. The relation between current and applied voltage is also characteristic of concentration polarization (6, 9, 10).

The object of the present work was to investigate the composition and properties of the layer of solution next to the anode, and by so doing to try and find out why one solution gives better polishing than another. The electrolytes studied were phosphoric acid solutions and mixtures of phosphoric acid with glycerol and ethylene glycol, these mixtures being chosen because they give better polishing than phosphoric acid alone (2). The greater part of the work consisted in measurements of viscosities, densities, and electrical conductances of solutions of cupric phosphate in these electrolytes. In addition, analyses of the anode layer and a few measurements of anodic polarization and limiting current were made.

Experimental

Materials

Phosphoric acid.—Baker's Analyzed, 85%.

Glycerol.—Baker's U.S.P.

Ethylene glycol.—Eastman Kodak No. 133.

Cupric phosphate, $CuHPO_4$.—This was prepared by a method not previously described. Cupric oxide was digested at 100° C with a solution of phosphoric acid, water, and ethylene glycol or glycerol, until no more black oxide was visible and a bulky blue precipitate had taken its place. This took half an hour or less. The mixture was left overnight, then filtered, and the precipitate (which was somewhat gelatinous) was washed, first with 95 per cent ethyl alcohol containing one-fourth its volume of 85 per cent phosphoric acid, then with 95 per cent ethyl alcohol. It

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was then extracted in a Soxhlet apparatus with 95 per cent ethyl alcohol to remove traces of phosphoric acid, and finally air-dried. The light blue powder was $CuHPO_4 \cdot H_2O$, as the following typical analyses show:

Sample No.	1	2	Theory, $CuHPO_4 \cdot H_2O$
%Cu	35.9	35.58, 35.68	35.80
%P	17.3	17.80, 17.66	17.45
Loss on heating to 150°C	11.2	11.6	10.15

Sample 1 was prepared using 68 ml (1 mole) 85 per cent phosphoric acid, 76 ml (1 mole) glycerol, 10 ml water, and 8 g (0.1 mole) cupric oxide. Sample 2 was prepared using 50 ml 85 per cent phosphoric acid, 46 ml ethylene glycol, 30 ml water, and 20 g cupric oxide. Other products were prepared by adding ethyl alcohol to solutions of cupric oxide in phosphoric acid and in phosphoric acid plus glycerol. They analyzed about 34 per cent Cu and 17.6 per cent P. A solution of cupric oxide in 50 per cent phosphoric acid, boiled with urea, gave a product with 34.6 per cent Cu and 17.8 per cent P.

TABLE I. *Composition of anode layer*

Expt. No.	Electrolyte in bulk			Anode layer		
	P_2O_5	H_2O	CuO	P_2O_5	H_2O	CuO
1*a*	1	6.75	0.013	1	6.43	0.20
1*b*	1	6.75	0.013	1	6.35	0.26
2	1	4.81	0.021	1	4.78	0.16

Units: formula weight ratios (1 formula weight P_2O_5 = 142 grams, etc.).

Before use, the salt was dehydrated to $CuHPO_4$ by heating to 140°–150° C. This product is hygroscopic.

Zinc phosphate, $ZnHPO_4 \cdot 2H_2O$.—This was made by a method analogous to the above. Analysis: 33.6% Zn, 15.0% P, 24.5% loss on ignition to 1000° C. Theoretical: 33.1% Zn, 15.7% P, 22.8% loss on ignition to 1000° C.

Calcium and sodium phosphates.—Secondary phosphates, reagent grades.

Analytical Methods

Phosphate was determined as $Mg_2P_2O_7$, copper electrolytically unless otherwise stated. Zinc was weighed as $Zn_2P_2O_7$.

Analysis of Anode Layer

Two sets of experiments were made. In the first, two copper plates, 5 cm x 4 cm, were hung vertically and parallel in a beaker of solution, and a potential of about 1.5 volts applied until the characteristic viscous layer had formed on the anode. The anode plate was then removed, drained for 5 seconds, wiped on the back (away from the cathode) and edges with filter paper, and the solution adhering to the anode then taken off with a rubber squeegee and analyzed. About 0.3 gram, or 0.2 ml, of solution was obtained from each test. The object of these rather crude experiments was to see if any marked change occurred in the ratio of water to phosphoric acid in forming the anode layer. The results are shown in Table I.

The second set of experiments was made to find the concentration of copper in the solution immediately next the anode. Attempts were made to find the solubility of copper phosphate in the various electrolytes by shaking the salt with the solutions for some time, then analyzing the solution, but the results were too erratic to be of any value. Since the information sought was the limiting concentration of copper in the anode layer, it was thought better to try and determine this directly. A flat copper cylinder, 3.5 cm in diameter and 1.5 cm high, was used as the anode. In the top surface was cut a shallow conical depression, 0.5 cm deep, and at the bottom of this depression a hole 2 mm wide and 2 mm deep was drilled. The copper block rested on the bottom of the cell during electrolysis, and the anode solution flowed slowly down the sloping conical face and into the hole. A potential of 1.5 volts was applied, which gave a current of about 0.1 amp. Samples of solution were withdrawn from the hole by a capillary pipette at intervals over a four hour period, and weighed; the copper content was determined either polarographically or by precipitation with α-benzoin oxime. The two analytical methods were consistent. The results are shown in Table II.

TABLE II. *Copper content of anode layer*

Electrolyte	Per cent Cu by weight	Grams Cu per 100 ml solution (estimated)
H_3PO_4, 85.8%	7.1, 6.1, 6.9, 6.0; avg 6.5	11.0
H_3PO_4, 77.2%	9.4, 9.7, 11.0; avg 10.0	15.9
H_3PO_4, 33.6%	9.1, 9.4, 8.8, 9.7; avg 9.3	11.2
Glycol + H_3PO_4(B2)	6.6, 6.4, 6.8; avg 6.6	9.4
B2 + 11% H_2O by vol.	6.7, 7.0, 6.7; avg 6.85	9.4
Glycol + glycerol + H_3PO_4 (C)	7.0, 7.3, 6.8; avg 7.0	9.9

Notes: 1. The symbols B2 and C refer to stock solutions; for composition see Table III.

2. The estimates of grams Cu per 100 ml solution were made with the help of density data reported below.

3. In all these tests the temperature was 29°–30°C.

Some of the anode layer samples deposited a blue solid if they stood for a few hours before analysis, notably those with 77 per cent H_3PO_4, solution B2 + 11 per cent H_2O, and solution C. Evidently, the anode layer is a *supersaturated* solution.

Viscosity Measurements

The most characteristic property of the anode layer is its high viscosity. The effect of added copper upon the viscosity of various phosphoric acid solutions was therefore determined. To simulate conditions in the anode layer as closely as possible, the copper was added as anhydrous $CuHPO_4$. Since this salt is rather hygroscopic, the copper content of the solutions was always checked by analysis.

TABLE III. *Composition of mixed solvents used*

Code	Composition
A	1 mole H_3PO_4 (86.2%) plus 1 mole glycerol (96.0%)
B1	1 mole H_3PO_4 (86.2%) plus 1 mole ethylene glycol (94.3%)
B2	1 mole H_3PO_4 (85.8%) plus 1 mole ethylene glycol (100%)
C	66 ml ethylene glycol, 100 ml glycerol, 166 ml 85% H_3PO_4, 35 ml water. (This is a typical electropolishing solution containing 1 mole of glycol and glycerol combined with 1 mole of phosphoric acid.)

Note: "1 mole H_3PO_4 (86.2%)" means an amount of 86.2% phosphoric acid—113.7 grams—containing one mole of H_3PO_4.

TABLE IV. *Flow times, densities, and absolute viscosities of solvents used*

Solvent	Density (D_4^{25})	Flow time	Viscosity at 25 °C
		sec	*centipoises*
H_3PO_4, 86.2%	1.695	213.8	46.8
H_3PO_4, 85.8%	1.690	201.6	44.13
H_3PO_4, 85.0%	1.682	194.8	42.42
H_3PO_4, 77.2%	1.592	110.9	22.58
H_3PO_4, 33.6%	1.205	243.3	2.60
H_3PO_4, glycerol (A)	1.4605	1820	346.0
A + 1.7% H_2O	1.452	1369	258.5
A + 8.0% H_2O	1.419	544.3	100.5
H_3PO_4-glycol (B1)	1.430	474.4	86.3
H_3PO_4-glycol (B2)	1.436	502	93.7
H_3PO_4-glycerol-glycol (C)	1.409	374.5	68.6

Note: Same viscometer used for all *except* 33.6% H_3PO_4.

Two Ostwald viscometers were used for the measurements. Each had an upper bulb of 7 ml volume and a capillary of length 20 cm, but one capillary had about half the radius of the other. The narrow capillary was used for the determinations with 33.6 per cent H_3PO_4, the wide capillary for the others. Ten ml of liquid were used for each measurement. The temperature was 25.00° + 0.02° C unless otherwise stated. Each viscometer was calibrated with two glycerol-water mixtures of measured density, the viscosities of these standard mixtures being found from the density using the tables of Bosart and Snoddy (5) and Sheeley (15), and the kinetic energy corrections being applied according to the formula of Poiseuille (3). The densities of the various solutions used, which were necessary to calculate the viscosities, were measured with a 5 ml pyknometer.

TABLE V. *Relative viscosities of $CuHPO_4$ solutions at 25°C*

Solvent	Per cent Cu by weight	Grams Cu per 100 ml solution	Density D_4^{25}	Relative viscosity
				η/η_0
H_3PO_4, 86.2%	0.424	0.606	1.709	1.06
	0.628	1.075	1.711	1.14
	1.100	1.90	1.729	1.28
	1.615	2.81	1.741	1.41
H_3PO_4, 85.8%	0.50	0.85	1.699	1.09
	1.05	1.80	1.712	1.23
	1.81	3.13	1.732	1.46
H_3PO_4, 85.0%	1.66	2.87	1.729	1.42
H_3PO_4, 77.2%	0.79	1.275	1.613	1.152
	1.56	2.54	1.633	1.335
H_3PO_4, 33.6%	0.75	0.925	1.2277	1.125
	1.35	1.68	1.2429	1.20
A	1.875	2.84	1.513	1.745
A + 1.7% H_2O	1.18	1.78	1.526	1.42
A + 8.0% H_2O	2.08	2.87	1.432	1.80
B1	0.97	1.41	1.456	1.275
B2	1.71	2.53	1.480	1.54
C	0.965	1.385	1.432	1.27
	1.65	2.20	1.452	1.51

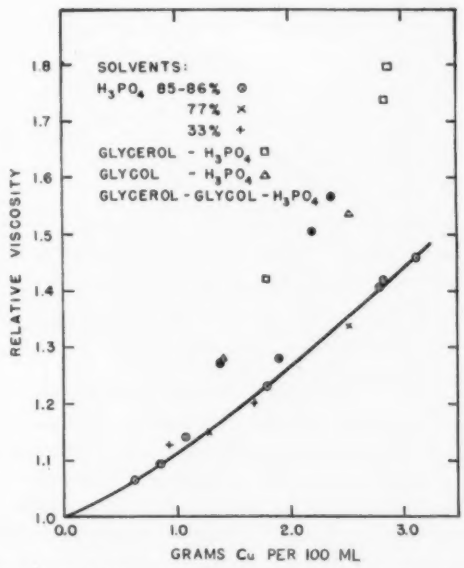

FIG. 1. Relative viscosity of copper phosphate solutions at 25°C.

The data are given in Tables III to V. To save space, only the relative viscosities are given for the copper salt solutions. Fig. 1 summarizes the relative viscosity data of Table V. Viscosity measurements with 85.5 per cent phosphoric acid as solvent and $CuHPO_4$ as solute were made at 18°, 35°, and 50° C

as well as at 25° C. The results are shown in Fig. 2. A few relative viscosities were measured with solutions of zinc, calcium, and sodium phosphates. These data are compared with those for copper phosphate in Fig. 3.

The probable error in the absolute viscosities is about 0.5 per cent, of which 0.2 per cent is due to uncertainties in calibration. That is, the values should be consistent among themselves to 0.3 per cent.

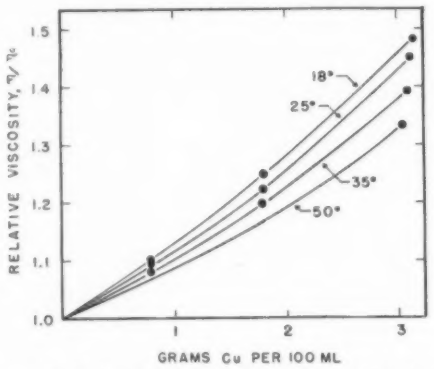

FIG. 2. Relative viscosity of copper phosphate in 85.8% phosphoric acid.

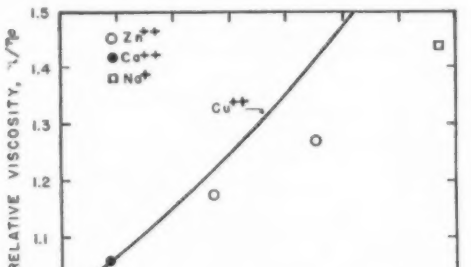

FIG. 3. Relative viscosities at 25°C: phosphates of Cu, Zn, Ca, and Na in 85–86% phosphoric acid.

Conductance Measurements

Although no abnormal effects were expected, it was desirable to measure the conductances of copper phosphate solutions of the kind which constitute the anode layer. Table VI shows the data obtained. By comparing conductances with viscosities it will be seen that the copper actually contributes to the conductance, that is, that the increase in viscosity caused by the copper is somewhat greater than the drop in conductance.

Measurements of Anode Polarization and Limiting Current

In most cases of electrolytic polishing, the current passing through the cell is independent of the applied voltage over a certain range. This effect has been described many times (6, 9, 10, 11, 16). However, previous workers have not obtained constant and stable currents in this range, because they have not used any stirring, and if the anode is at rest with respect to the solution, the diffusion layer, which determines the limiting current, keeps on growing until it is dissipated by convection currents.

In this work the anode was kept in motion while current-voltage curves were plotted. It was a vertical copper rod, 6 mm diameter, covered with insulating lacquer except over a cylindrical area 18 mm long which was immersed in the solution. The rod was rotated at a fixed speed. The cathode was a copper sheet about 20 mm wide, bent around the anode in the form of a cylinder some 8 cm in diameter. To measure the polarization of the anode, a copper wire was mounted vertically about 2 mm away from the anode. The arrangement of the cell and the electrical circuit are shown in Fig. 4. The cell was surrounded by a water bath for temperature control. Phosphoric acid-water mixtures containing known proportions of copper were used as electrolytes, and three different rotation speeds were obtained by use of different sized pulleys.

TABLE VI. *Conductance of copper phosphate solutions at 25°C*

Solvent	Grams Cu per 100 ml solution	Specific conductance k	Viscosity η	$k\eta$
H_3PO_4 (86.8%)	0.0	0.0888	46.8	4.17
	1.075	0.0811	53.1	4.31
	1.90	0.0714	59.5	4.25
	2.81	0.0700	65.8	4.61
H_3PO_4 (85.0%)	2.87	0.0753	60.7	4.58
Glycerol-H_3PO_4	0.0	0.0105	259	2.72
(A + 1.7% H_2O)	1.78	0.0075	368	2.76

Current-voltage curves of the type shown in Fig. 5 were obtained. On starting the stirring motor and closing the electrolysis circuit, the current, at first quite high, would drop very rapidly in the first few seconds, and would continue to fall for some time, perhaps for half an hour or more. If the applied voltage was less than 1.6–1.7 volts, the current eventually became constant and was then absolutely steady; it would not change when the voltage was changed within the range of the flat portion AB of Fig. 5. This current, which we call the *limiting current*, is definite and reproducible.

At the same time that the current was measured, so was the potential difference between the anode and the stationary copper wire close to it, using the potentiometer P (Fig. 4) for this purpose. This represents the polarization emf of the anode, subject to a

very small correction for the ohmic potential drop between the anode and the wire. A part of the polarization (10–50 millivolts) is due to the difference in cupric salt concentration; the rest is the excess positive potential on the anode due to the fact that the metal is not in equilibrium with the solution in contact with it. This emf was quite reproducible while the limiting current was passing, though of course it depended on the applied voltage.

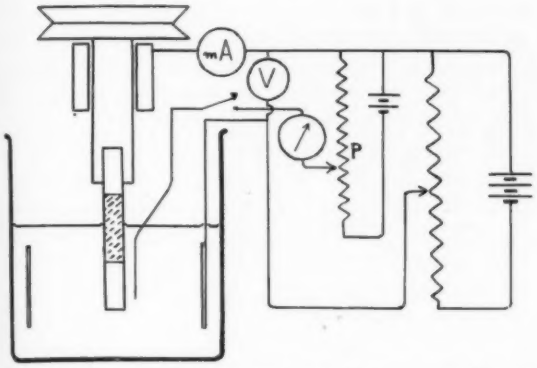

FIG. 4. Apparatus for measuring anode current and anode polarization.

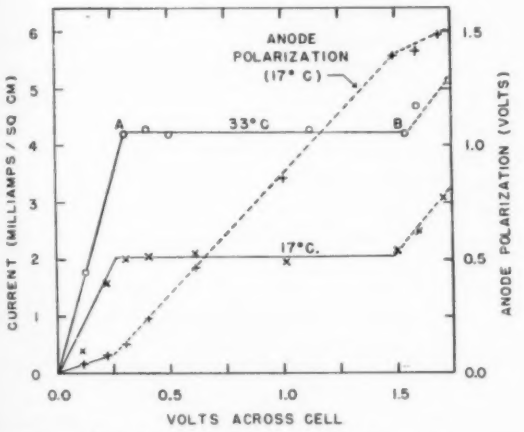

FIG. 5. Sample anode current and polarization curves (rotation speed, 1.75 rps; electrolyte, 86% H_3PO_4 plus 1.8% Cu).

If the voltage was increased beyond the point B (Fig. 5) the current began to rise and continued to rise even when the voltage was held constant, the polarization meanwhile falling. Simultaneously, bubbles of oxygen were seen at the anode. The diffusion layer at the anode is disturbed by these bubbles, and both the current and the polarization become very erratic. The point B can be located very accurately, and it came at an anode polarization of 1.45 volts in all the tests, regardless of electrolyte concentration, temperature, or stirring speed. This constancy is to be expected, since point B marks the onset of a new anodic process, oxygen discharge.

The point A is much harder to locate, as the anode layer is formed so slowly and it takes so long for the current to reach a constant value. No attempt was made to locate it accurately, but it appeared that below an applied potential of about 0.25 volt, depending on the speed of rotation, the steady current is less than the limiting current, and the anode polarization is very small. In this region no electrolytic polishing takes place; the anode is etched.

Table VII gives the limiting currents which were obtained under various conditions. For comparison, the approximate viscosities of the solutions forming the bulk of the electrolyte are given also. Unfortunately, the viscosities of the actual solutions used were not determined; the viscosities were estimated from the composition and other data available. These data are strictly preliminary.

TABLE VII. *Limiting currents*

Electrolyte	Speed rps	Temp °C	Current, ma	Approximate viscosity, centipoises	$I\eta$
86% H_3PO_4 plus 1.8 g Cu/100 ml of solution	1.75	17	6.8	75	510
	1.75	21	9.0	64	580
	1.75	25	11.0	53	580
	1.75	33	14.0	41	570
	2.6	21	11.8	64	750
	3.4	21	15.1	64	1140
81% H_3PO_4 plus 1.7 g Cu/100 ml	2.6	27	23	35	800
76% H_3PO_4 plus 1.5 g Cu/100 ml	2.6	26	37	23	850
76% H_3PO_4 plus 2.1 g Cu/100 ml	2.6	13.5	21	42	880
	2.6	20	30	32	960
	2.6	27.5	35	24	840
	2.6	35	44.5	19	840

Discussion

General

All the results of this work are consistent with the view that the electrolytic polishing of copper in phosphoric acid is due to the pressure of the viscous layer at the anode, which controls the rate of dissolution by controlling the rate at which the product of anodic dissolution—copper phosphate—can diffuse away. It will diffuse faster where the layer is thin and the concentration gradient high, that is to say at the elevated parts of the anode surface, and more slowly at the depressed parts where the layer is thick. Moreover, diffusion from a convex surface will be faster than from a flat surface covered by a diffusion layer of the same thickness. Diffusion, not

electrical (ohmic) resistance, seems to be the governing factor. The solution is a good conductor, even in the anode layer, and, therefore, the copper salt must move away from the anode by diffusion rather than by electrical transport. The action is like that of a polarograph in reverse, with phosphoric acid the "supporting electrolyte." The current-voltage curves show this very clearly, for as the voltage is increased from zero, electrolytic polishing begins only when the flat portion, characteristic of concentration polarization, is reached. The increase in limiting current which is produced by increasing the speed of rotation of the anode is also characteristic.

A striking qualitative test which shows that a diffusion layer is necessary for electropolishing is to use a horizontal disk of copper or brass as the anode and rotate it rapidly during electrolysis. If rotation is fast enough there is polishing only in the middle of the disk; outside a sharply defined radius there is etching instead of polishing, because here the linear velocity is so great that because of turbulence the diffusion layer cannot form. By increasing the applied voltage to make the copper dissolve faster, the zone of polishing can be extended.

Polishing occurs at voltages higher than that of point B, Fig. 5, but the bubbles of oxygen which are formed in this range disturb the diffusion layer and make the surface irregular; it is still bright, but it no longer reflects objects as clearly as the more mirror-like surface produced in the range AB. In this range a *gaseous* anodic film may contribute to the polishing (see Faust, 1949, ref. 8). In fact, examples of electropolishing are known where no flat current-voltage curve, characteristc of a liquid diffusion layer, is observed.

The Viscosity of the Anode Layer

The high viscosity of the anode layer means that this layer can be thin and yet firmly attached, so that it is not swept away by ordinary convection currents. We may, therefore, expect a correlation between the efficiency of electrolytic polishing and the viscosity of this layer.

Facts relating to electrolytic polishing are:

(*a*) Aqueous phosphoric acid solutions are effective in electropolishing copper and brass in concentrations above about 30 per cent H_3PO_4 (9).

(*b*) Mixtures of phosphoric acid with glycerol or ethylene glycol, or both, are more effective than phosphoric acid alone (2).

(*c*) The optimum temperature range for polishing in these solutions is 20°–40° C. At higher temperatures the polishing efficiency falls off very rapidly; at lower temperatures the conductivity is not high enough (11).

(*d*) The specimen is polished better if it is moved through the solution at a moderate, steady speed than if it is at rest (2).

(*e*) Pure zinc is not polished at all in these solutions under conditions where copper, brass, steel, and other metals are polished (17).

The viscosities which are reported in this paper show the following relationships:

(1) Dissolved copper phosphate raises the viscosity of phosphoric acid solutions. The relative viscosity, η solution/η solvent, depends on the mass of copper per unit volume of the solution, but *not* on the concentration of phosphoric acid within the range studied. The relative viscosity increases rather faster than linearly with the copper concentration. It is affected by temperature, being greater at low temperatures than at high.

(2) The relative viscosity of copper phosphate solutions in mixtures of phosphoric acid with glycerol, glycol, or both is significantly greater than that of solutions in phosphoric acid having the same concentration of copper.

(3) The relative viscosity of solutions of zinc phosphate is significantly lower than that of copper phosphate solutions.

Apparently there is a correlation between the slope of the relative viscosity-concentration curve and the efficiency of electropolishing, since the mixtures with glycerol and glycol polish better than phosphoric acid alone, high temperature gives poor electropolishing, and zinc is not polished in these solutions.

The maximum concentration of metallic salt in the anode layer will also affect the thickness and tenacity of the layer, but from the data of Table II there seems to be little difference between different solvents in this respect.

The Magnitude of the Limiting Current

Let us suppose that next to the anode surface there is a sharply defined layer, which we shall call the diffusion layer, within which the concentration of metal salt varies with the distance from the surface. Outside this layer the concentration is assumed to be uniform. This simplified picture of the boundary layer in concentration polarization is used by Nernst (14), Agar and Bowden (1), and others. We shall assume that the thickness of this layer is independent of the salt concentration in the bulk solution. (Agar and Bowden show that this will be so if the solution is stirred, though they consider the viscosity to be the same everywhere.) We shall also assume that the diffusion rate varies inversely as the viscosity, that the viscosity is a linear function of concentration, and that the metal salt moves only by diffusion, not by electrical migration.

Let d = thickness of diffusion layer.
η_0 = viscosity of solvent.
$\eta = \eta_0 + \alpha c$ = viscosity of a salt solution of molar concentration c.
c_s = molar concentration of salt at the anode surface.
c_0 = molar concentration of salt in the bulk solution.
$D = k/\eta$ = diffusion coefficient of salt.
I = current density.
F = the faraday.
n = the oxidation number of the metal in solution = 2 for copper.

Then at a distance x from the anode surface, within the diffusion layer, diffusion rate $= -D\frac{dc}{dx}$ per cm²

$$= -\frac{k}{\eta_0 + \alpha c}\frac{dc}{dx}$$

$$= \frac{I}{nF}.$$

Rearranging,

$$\frac{dc}{\eta_0 + \alpha c} = -\frac{I}{nFk}\,dx$$

$$\int_{c_s}^{c_0}\frac{dc}{\eta_0 + \alpha c} = -\int_0^d \frac{I}{nFk}\,dx$$

$$\frac{1}{\alpha}\ln\frac{\eta_0 + \alpha c_0}{\eta_0 + \alpha c_s} = -\frac{Id}{nFk}$$

or,

$$I = \frac{nFk}{\alpha d}\ln\frac{\eta_0 + \alpha c_s}{\eta_0 + \alpha c_0} \qquad \text{(I)}$$

All of the quantities in equation (I) are known, or can be measured by the methods described in this paper, except k and d. We can get a provisional value for k by the very questionable assumption that the effective size of the cupric ion in the phosphoric acid is the same as that in water, i.e., that k is the same in both solvents, and by the equation

$$D = \frac{RT}{nF^2}\lambda_0$$

where λ_0 is the specific ionic conductance of Cu^{++}, and D its diffusion coefficient, both in water. At 25° C, λ_0 is about 54, whence $D = 7.3 \times 10^{-6}$ cm²-sec⁻¹, and $k = 6.5 \times 10^{-8}$ dynes. Taking the case of 76 per cent phosphoric acid containing 1.5 grams Cu in 100 ml, with rotation speed 2.6 rps and temperature 26° C, the distance d is calculated to be *0.006 cm*. This is a reasonable order of magnitude. For effective electrolytic polishing, d should be about the same as the height of the irregularities to be removed.

The Limiting Current and Electropolishing Efficiency

A measure of the speed of electropolishing, that is, rate of removal of projections on the anode surface, might be the quantity dI/dd, since the diffusion layer is thinner over the projections. We have

$$\frac{dI}{dd} = -\frac{nFk}{\alpha d^2}\ln\frac{\eta_0 + \alpha c_s}{\eta_0 + \alpha c_0} \qquad \text{(II)}$$

From equation (II), a large α would apparently lead to poor electropolishing, whereas the reverse is true in practice. Of course, the larger α is, the smaller is the limiting diffusion current, and this fact, in itself, would give slower electropolishing. However, a large α probably means a thinner and more tenacious diffusion layer, and from equation (II), a small d favors fast electrolytic polishing. A large α also means that c_0, the concentration of metal salt in the bulk of the electrolyte, can become relatively high before the electropolishing effect ceases.

A proper quantitative theory of electropolishing requires that the effective thickness of the boundary layer be known. Levich (13) has shown how to calculate this for moving electrodes of simple geometry where the diffusion constant does not vary with concentration. The calculation for the electropolishing case will be much more difficult, especially since the relation between viscosity and concentration should really be expressed by a quadratic.

Constitution of the Copper Phosphate Solutions

An interesting question which arises from this work is: Why do copper salts raise the viscosities of these solutions? One explanation is that the cupric ions become hydrated and, therefore, raise the effective concentration of the phosphoric acid. However, to produce the effects observed, one cupric ion would have to hydrate with 12 molecules of water in 85 per cent phosphoric acid, and with 30 molecules of water in 33 per cent acid. (These estimates are based on the author's viscosity measurements of aqueous phosphoric acid solutions, which will be published later.) Another possibility is that copper combines covalently with phosphoric acid to link two or more molecules together. This is rather likely, in view of the effect of temperature on the relative viscosity, and of the fact that the electrode potential of copper in aqueous cupric sulfate solution is depressed considerably by adding phosphoric acid. Probably both effects are operative. We hope to get more information on this point by measuring polarographically the diffusion constant of cupric ions in these solutions. We shall then be in a better position to test equation (I).[2]

[2] Miss Ruth Holzinger, of this laboratory, is measuring the polarographic diffusion current of cupric copper in con-

Summary and Conclusion

The subject of investigation was the layer of solution formed at the anode during the electrolytic polishing of copper in phosphoric acid and in mixtures containing phosphoric acid. The composition of this layer, especially the limiting concentration of cupric salt next to the anode surface, was found by analysis. The viscosity relations within the layer were studied by preparing copper phosphate solutions of known composition and measuring their viscosity and density. In a few cases their electrical conductivity was measured also. For use in making these solutions, the salt $CuHPO_4$ was prepared by a method not hitherto published.

The addition of the copper salt increases the viscosity considerably. The effect can be represented approximately by an equation

$$\frac{\text{viscosity of solution}}{\text{viscosity of solvent}} = 1 + Ac$$

where c is the weight of copper per unit *volume* of solution, and A is a constant. For aqueous phosphoric acid solutions A is independent of the phosphoric acid concentration over a wide range. For mixtures of phosphoric acid with ethylene glycol or glycerol, A has nearly double its value for phosphoric acid alone, that is, dissolved copper raises the viscosity of these mixtures much more than it raises the viscosity of phosphoric acid. Electrolytic polishing is also better in these mixtures than in phosphoric acid alone. The factor A falls with rising temperature, and so does the electropolishing efficiency.

Preliminary studies were made of the current-potential relationships at a copper anode in the form of a rotating cylinder. Characteristic curves were obtained in which the current is independent of the applied voltage over a certain range. The dependency of this "limiting current" on the solvent, copper concentration, rotation speed, and temperature was noted, and the data agreed with the hypothesis that the rate of dissolution of the anode is limited by the diffusion of copper salt through a boundary layer. An equation was derived for the limiting current in terms of the thickness of this layer; from the observed current, a reasonable value of the boundary layer thickness was calculated.

For rapid and effective electropolishing, the anode layer should have a depth comparable with that of the surface irregularities, that is, it should be very thin, and it should be tenaciously held. The ideal electrolyte for the purpose would have a low viscosity which was greatly increased by adding metal salt, and the metal salt would be very soluble in it. Steady agitation improves electrolytic polishing by thinning down the anode layer.

centrated phosphoric acid solutions. The first results show that the product of diffusion constant and viscosity in such solutions is only one-tenth that in water. That is, the effective radius of the cupric ion, or complex, is considerably greater in phosphoric acid than in water.

Acknowledgment

The stimulus for the work described here came from a project of the Engineering Experiment Station of the University of Colorado, sponsored by Shwayder Brothers, Inc., of Denver, and relating to the electropolishing of brass. The writer is indebted to Mr. W. G. Axtell, Chief Engineer, Shwayder Brothers, for his friendly interest.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1951 issue of the Journal.

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Improvements in the Electrowinning of Chromium[1,2]

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ABSTRACT

Improvements in the electrowinning of chromium from trivalent or "chrome alum" solutions, made since publication of a previous paper, are disclosed. Elimination of sodium sulfate from the electrolyte and changes in cell design have decreased the cost of electrowinning chromium metal. Details of the new cell design and data obtained with a 120-pound-per-day cell are discussed.

The sensitivity of laboratory-size cells to certain critical impurities and other variables tends to obscure the possibilities of this type of electrolyte. Research in pilot-plant cells has shown that proper cell design and operation on a sufficiently large scale can largely overcome the sensitivity of chromium sulfate electrolytes to impurities and, to a lesser extent, to pH and other variables.

Introduction

Since publication of previous reports (1) on the electrowinning of chromium from trivalent solutions, extensive work has been done on simplifying the electrolyte and the electrolytic cell. The purpose of this work has been to decrease the cost of producing electrolytic chromium by decreasing both plant construction and operating costs.

Preparation of cell feed has been simplified by dispensing with sodium sulfate from the electrolyte, which not only eliminates the problem of recovering the sodium salt but also results in easier cell control. Cell feed consists solely of a concentrated solution of chromium ammonium alum.

The early pilot-plant cell (2) met the complex requirements for successful deposition of metal, but it was expensive to construct and proved to be relatively difficult to operate because of the necessity for continuously operating several pumps. Experiments with a series of cells of more conventional design resulted in the development of a simplified cell with better operating characteristics. The improved cell design and new electrolyte, plus a further study of operating variables, have substantially increased the tolerance of the cell to critical impurities and have made production of heavier deposits a practical operation.

Production of electrolytic chromium is one phase of the Bureau of Mines study on the economic utilization of substandard domestic chromium ores.

Cell Construction

Design Requirements

The successful electrodeposition of chromium at a high current efficiency from chromium sulfate solutions requires control of the pH between relatively narrow limits and conservation of the divalent chromium formed at the cathode. Diaphragms are essential, not only to prevent the sulfuric acid formed at the anode from mixing with the catholyte but also to prevent the chromic acid formed at the anode from oxidizing the divalent chromium. In addition to preventing the anolyte from mixing with the catholyte, the diaphragm must control the quantity of catholyte that flows into the anolyte. The ideal diaphragm, therefore, is one with a limited and uniform porosity.

The quantity of catholyte flowing into the anolyte controls the pH by controlling the ammonium ion concentration of the anolyte. If the highly acid anolyte does not also contain ammonium ion, the transference rate of hydrogen ion into the catholyte is greater than the evolution of hydrogen at the cathode and the pH of the catholyte drops. In other words, if the ammonium ion concentration of the anolyte is increased, the pH of the catholyte will increase and vice versa.

A further requisite for deposition of metal is a rapid but nonturbulent flow of electrolyte over the cathode surface.

Anode Compartments

The anode compartment of the new cell, shown in Fig. 1, meets the essential requirements of an anode holder or frame, anolyte chamber, diaphragm, and diaphragm support in one self-supported unit. It consists of a frame fabricated from strips of 1-inch (2.54 cm) and $\frac{3}{8}$-inch (0.95 cm) Lucite or Plexiglas sheet with a No. 17 Vinyon cloth diaphragm cemented to each side. Two outlets are provided for circulating anolyte to a common header. The compartment was designed to minimize machining of Lucite, an important cost item. Lucite strips are cut from polished sheets with a circular power saw and cemented together on the polished surfaces. The

[1] Manuscript received February 3, 1950. This paper prepared for delivery before the Buffalo Meeting, October 11 to 14, 1950.

[2] Papers by the staff of the U. S. Bureau of Mines are not subject to copyright.

$\frac{3}{8}$-inch (0.95 cm) strip is left out of the top side, except for a small piece in the center, and is lapped with the 1-inch (2.54 cm) strips at the corners to make a tongue-and-groove joint. The only machining required is drilling of the circulation outlets and, occasionally, sanding of a projecting corner joint to give a relatively flat surface for the diaphragm. The outlets are extended by cementing short lengths of Lucite tubing to the frame.[3]

Each compartment holds one anode, which consists of a split sheet of lead-1 per cent silver alloy burned to a lead-covered copper header bar, as shown in Fig. 1. The alloy sheet is split vertically so as to pass by the brace at the center of the top Lucite strips, and is suspended freely in the compartment except for the bottom edge which is centered between the diaphragms by a bottom groove.

No. 17 Vinyon is sufficiently heavy and resistant to stretching so that no diaphragm bracing is required; bracing is necessary with lighter fabrics. Untreated No. 17 Vinyon also has a lower and more uniform electrical resistance than the coated or preshrunk diaphragms previously used.

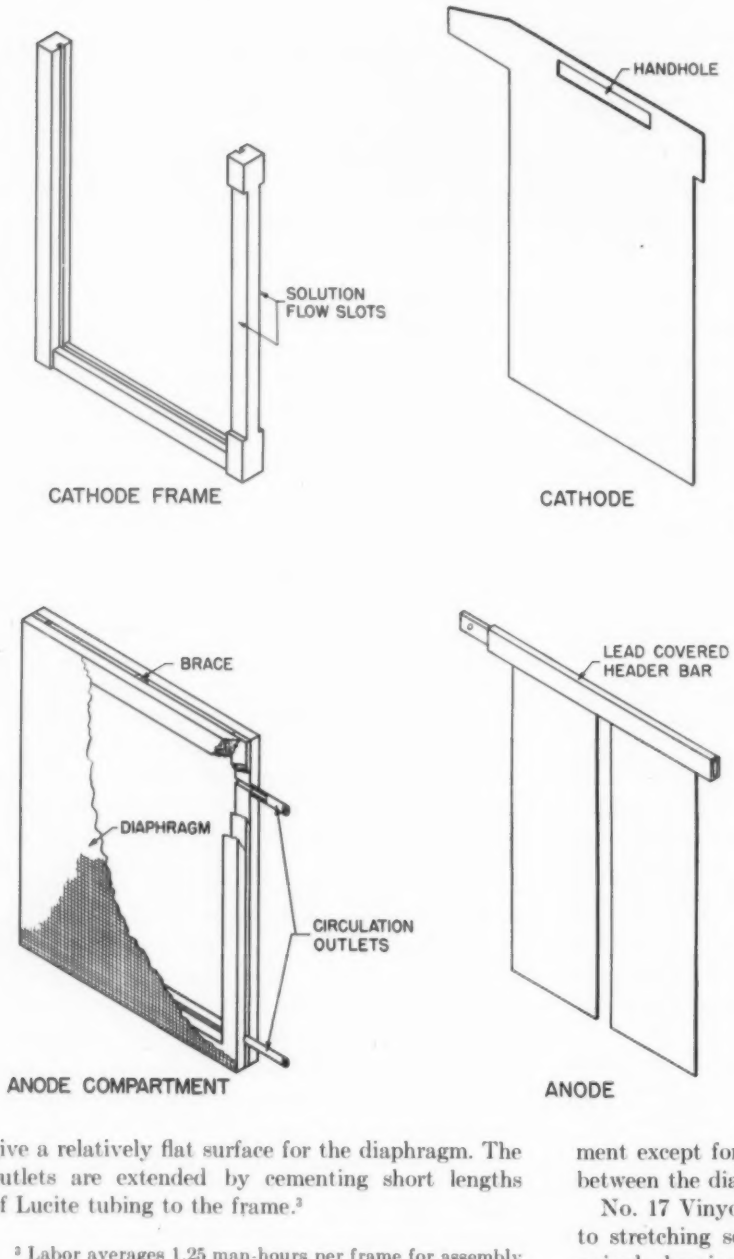

FIG. 1. Details of cathode frame, cathode, anode compartment, and anode.

[3] Labor averages 1.25 man-hours per frame for assembly and 0.75 man-hour for cementing the diaphragm in place. Specialized equipment could decrease these costs. Cost of Lucite, cement, and Vinyon diaphragms averages $24.13 per anode compartment.

Oxygen generated in the compartment escapes through the narrow slit between the anode and the top Lucite strips. Acid spray carried by the escaping gas impinges on the overhanging lead-covered anode bar and any not removed is deflected toward the ventilating system.

Cathode Frames and Cathodes

The cathode frame, also shown in Fig. 1, is fabricated from Douglas fir. The fir strips are cut $2\frac{1}{4}$ inches (5.71 cm) wide from standard 2-inch (5.08 cm) timber and are fastened together with monel screws. The bottom strip and one upright strip are cut on the sides to provide flow slots for free circulation of catholyte from the cell tank, when the cathode frames are assembled with the anode compartments. Evolution of hydrogen at the cathode causes a rapid, but controlled, circulation of catholyte in at the bottom and out the side of the frame. The importance of rapid, uniform circulation cannot be overemphasized. The effect of rapid movement of the catholyte is to maintain the pH at the cathode surfaces more nearly uniform and closer to the pH of the body of the solution. The result is a wider pH range for efficient plating and a greatly increased tolerance to impurities. The concentrations of some critical impurities, such as aluminum and lead, in the standard pilot-plant electrolyte, are five to ten times as great as those which can be tolerated in laboratory cells.

Average cathode-to-diaphragm distance has been increased from 0.7 to 1.1 inches (1.78 to 2.79 cm). The result is an increase in cell potential of 0.33 volt, but the increased power cost is more than offset by decreased labor costs. The wider spacing means better circulation of catholyte, less straightening of cathodes, and heavier deposits. In addition to the advantage of removing the cathodes for stripping less often, the heavier deposits are easier to strip and are more attractive to the prospective consumer.

Cathode plates are ordinarily type 316 stainless steel, and each plate has 7.5 ft^2 (70 dm^2) of submerged area. The area was reduced from 10 ft^2 (93 dm^2) because the larger plate with deposited chromium was too heavy to handle by hand. The cathodes measure $20\frac{1}{2}$ by 34 in. (52.1 by 86.4 cm) overall, including the hand-hole at the top. They should have been made 20 by 36 in. (50.8 by 91.4 cm) to obtain maximum utilization of standard stainless steel sheet. Aluminum cathodes with integral header bars or connector lugs are being tried on an experimental basis. The cathode shown in Fig. 1 is of this type. The integral cathode was designed to avoid the problem of protecting copper header bars from cell spray, but it is also cheaper, lighter, and easier to handle than a conventional-type cathode. Chromium deposited on aluminum has a darkened surface next to the plate, and the aluminum plates are more difficult to maintain than stainless steel, but the lower cost and lighter weight may outbalance the disadvantages. Sodium-free electrolyte does not attack the cathode plates at the solution line.

Cell Assembly

The cell is assembled by starting with an anode compartment in one corner of the cell tank and alternately placing cathode frames and anode compartments until all the frames are in place. The assembly requires one more anode compartment than cathode frame, and the two unused outside diaphragms are made impervious to solution flow. Fig. 2 is a photograph of a 10-cathode, 120-pound-per-day cell being assembled. Two anode compartments and two cathode frames are in place. The numbers are placed on the following parts: (1) top edge of anode, (2) cathode, (3) anode bus, (4) cathode bus, (5) anolyte header, (6) ventilation hood, (7) heat exchanger, and (8) flexible connection to anolyte header. The bottom supports for the frames are made of fir and are slotted to maintain the proper positions of the anode compartments and cathode frames. The slots are $2\frac{1}{2}$ inches wide (6.35 cm), and spaces between the slots are $2\frac{1}{4}$ inches (5.72 cm). This arrangement spaces the cathodes on $4\frac{3}{4}$-inch (12.1 cm) centers and leaves a $\frac{1}{8}$-inch (0.32 cm) space for each set of frames to allow for uneven frame strips. After all of the frames are in place, a top spacer bar is placed in position. This bar may be seen in Fig. 3, a photograph of the completed cell in operation. Also visible in Fig. 3 are (9) anolyte overflow, (10) catholyte overflow, and (11) immersion pH assembly. This assembly is a standard unit for indicating pH continuously and is equipped with high-temperature glass and calomel electrodes and a resistance thermometer. The cathodes shown in Fig. 3 are stainless steel, with copper header bars. The copper bars and rivets are covered with various experimental protective coatings, as follows: 1 thermoplastic resin, 5 aluminum metal spray, 2 lead spray, and 2 stainless steel spray.

The heat exchanger is fabricated of Karbate pipe and is mounted on the side of the anolyte header where the flow of catholyte is maximum. The cathode frames are elevated from the bottom of the cell tank to allow for free circulation of catholyte and to provide a space for accumulation of insoluble residue. At rare intervals large pieces of metal will separate from a cathode while still in the cell, and if a space is not provided for the metal to fall free of the frame it is necessary to shut the cell down to remove the metal before another cathode can be inserted in the frame. The space at the end of the cell is useful in

assembling the cell, while both the bottom and end spaces increase the volume of the catholyte. A large catholyte volume helps to stabilize the pH, the chromium concentration, and the specific gravity.

The anolyte overflow pipe is connected to the anolyte header inside the cell, and the level of the anolyte can be changed readily by a slight turn of a pipe cap on the overflow. Correct flow of catholyte into the anolyte is obtained, ordinarily, when the level difference is about 0.3 inch (0.76 cm). Excess catholyte flows out of the catholyte overflow. Water is added to the anolyte head tank to keep the specific gravity lower than that of the catholyte.

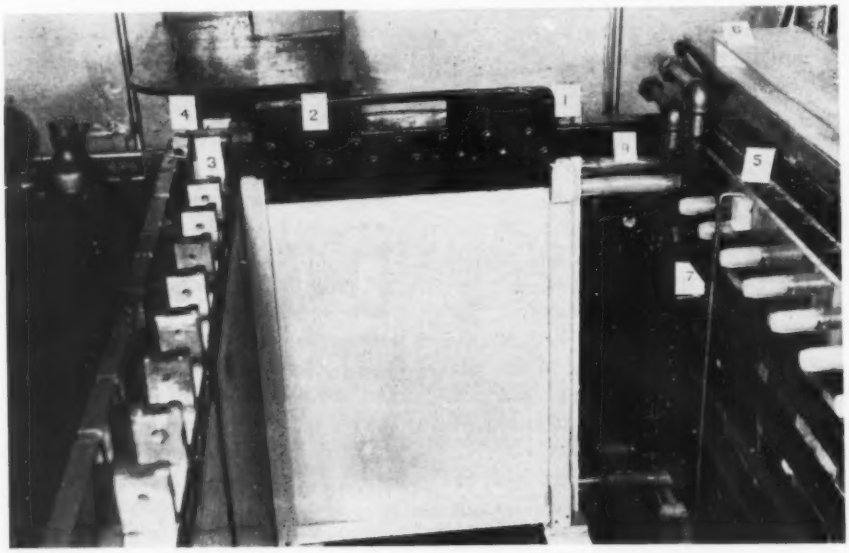

FIG. 2. Ten-cathode cell being assembled

FIG. 3. Chromium electrowinning cell in operation

OPERATING DATA

The cell feed contains chromic sulfate and ammonium sulfate in the proportions existing in the alum, $(NH_4)_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$; the catholyte solution contains chromous sulfate, chromic sulfate, and ammonium sulfate; and the anolyte contains chromic sulfate, chromic acid, ammonium sulfate, and sulfuric acid. Typical analyses of the three solutions are shown in Table I.

In addition to the essential constituents shown, the cell feed normally contains the following impurities in g/l: iron, 0.3 to 0.5; aluminum, 0.05 to 0.5; lead, 0.02 to 0.03; calcium, 0.03; magnesium, 0.01; titanium, 0.008; vanadium, 0.05; manganese, 0.01; copper, 0.001; nickel, 0.003; molybdenum, 0.0003; and silica, 0.03. Analyses of the deposited metal show 0.1 to 0.4 per cent iron and may show spectrographic traces of calcium, magnesium, aluminum, silicon, lead, and copper. A 60-pound-per-day cell has been operated for extended periods, using alum crystals and water for cell feed, but the previously prepared solution is more convenient.

A previous paper (1) described the catholyte then in use as a chromium sulfate-ammonium sulfate-sodium sulfate electrolyte, and discussed the necessity for periodically adding a soluble sulfite to obtain an adherent deposit at a reasonable current efficiency. This electrolyte produced good deposits and was used for all original development work on the process. However, the necessity for adding sodium sulfate to

cell feed prepared from chromium ammonium alum proved to be an important cost item and every effort was made to eliminate sodium as an essential catholyte constituent. It was successfully eliminated partially by increasing the ammonium sulfate concentration and partially by a better understanding of the effect of such variables as catholyte temperature and rate of circulation. The mechanism whereby sulfite additions modified the character of the deposited metal in the original process has not been definitely determined but, in the quantities previously used, sulfite appears to be entirely without effect in the present process.

It is essential that the ammonium sulfate concentration of the catholyte be maintained at more than 80 g/l NH_3 for the best results. This control is accomplished by regulating the concentration of the cell feed. One advantage of the two-component electrolyte is that the ammonium sulfate concentration can be approximated when the chromium analysis and specific gravity are known. The large differential in the NH_3 concentration of the cell feed and the catholyte is a measure of the ammonium-ion transference from the anolyte, although about 5 g/l is the result of concentration by evaporation of the catholyte. The total chromium concentration of the catholyte can vary considerably, but it is normally held at 40 g/l, plus or minus 3 g/l, to facilitate maintaining the proper specific-gravity differential between the anolyte and catholyte. An increase in chromium concentration of the catholyte increases the adherence of the metal to a minor extent, while a decrease below 35 g/l may cause a drop in current efficiency. If the chromium concentration of the catholyte is held at 40 g/l, the distribution of chromium entering the cell in the feed is 72.7 per cent plated on the cathodes, 20 per cent in the anolyte overflow, and 7.3 per cent in the catholyte overflow.

TABLE I. *Typical analyses of cell feed, catholyte, and anolyte solutions, grams per liter*

	Cr				NH_3	H_2SO_4
	Total	+6	+3	+2		
Cell feed	132	Nil	132	Nil	43.2	—
Catholyte	40	Nil	17	23	90.0	—
Anolyte	22	20	2	Nil	18.0	290

Other cell operating data are shown in Table II. The current efficiency is based on deposition from the trivalent state since the cell feed contains only trivalent chromium. The addition agent, Goulac, is a lignin sulfonate and is added to maintain a protective froth over the catholyte. Froth holds down spray and inhibits atmospheric oxidation of the divalent chromium. At the current density and current efficiency shown, a 73-hour plate will weigh 5 lb/ft² (0.25 kg/dm²) and vary in thickness from 0.15 to 0.20 inch (0.38 to 0.51 cm). If the current density is cut to 67 amp/ft² (7.2 amp/dm²), the time of deposition can be extended to 96 hours for a deposit which averages 5.5 lb/ft² (0.27 kg/dm²). The principal disadvantage of the lower current density is lower production per cell, but this may be offset by lower cell voltage and lower power costs. At 67 amp/ft² (7.2 amp/dm²) the power consumption is about 5.0 kwhr/lb of metal.

The temperature of the catholyte must be 46°C or higher for optimum current efficiency, and operation at still higher temperatures has some advantages. Tolerance of the catholyte to heavy-metal impurities, such as lead, increases, and the sulfur and iron analyses of the finished metal decrease with increasing temperature. A solution containing 30 mg/l of lead gives a current efficiency of 60 per cent at 60°C, but only 52 to 53 per cent at 50°C. The permissible pH range for optimum deposition increases with increasing temperature and the decrease in sulfur and iron is a result of a higher operating pH. Chromium deposited at 60°C is not as bright as metal deposited at 50°C, but the deposit is more uniform.

TABLE II. *Cell-operating data*

Current density	80 amp/ft² (8.6 amp/dm²)
Cell potential	4.8 volts
Current efficiency (Based on $Cr^{+3} \rightarrow Cr^0$)	60%
Kwhr/lb metal	5.6
pH	2.45 to 2.65
Temperature	59 ± 1°C
Time of deposition	72 to 80 hours
Addition agent	0.03 g Goulac/liter of cell feed

At 60°C, a pH range of 2.3 to 2.35 results in a sulfide sulfur content averaging 0.03 per cent, while a pH range of 2.5 to 2.6 results in a sulfur content averaging 0.01 per cent. A previous paper showed that a pH averaging 1.86, at 32.3°C, resulted in a sulfur content of 0.07 per cent. Since a decrease in current density results in a decreased pH at the plating surface, any thin spots on a cathode caused by an excessively bent cathode plate results in metal which contains higher sulfur and iron than the average. The high-current-density metal on the opposite side of the plate contains less sulfur and iron than the average.

At 60°C the lower limit for pH is about 2.3. Below this limit, the current efficiency drops and deposition may completely stop and then restart at intervals, causing a striated metal. This phenomenon is caused by the fact that the instant deposition

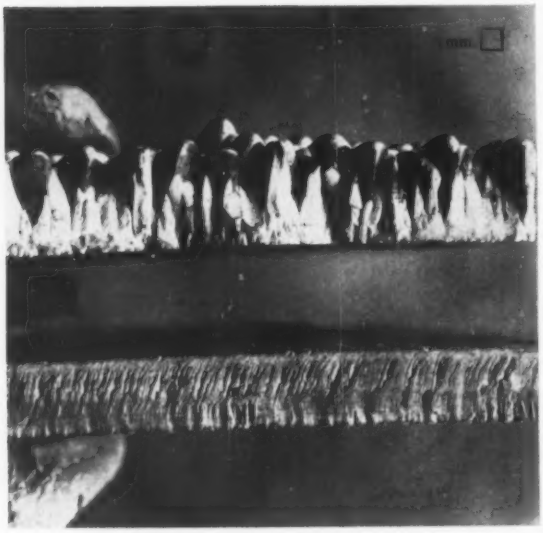

FIG. 4. Macrocamera photograph of two representative chromium deposits.

stops the increased evolution of hydrogen causes the pH to rise sharply, and deposition starts again in 10 to 30 minutes. Sharp depolarization and, later, repolarization of the cathode may be readily seen on the chart of a current-potential recorder. The upper pH limit is less sharp and operation at a pH up to 2.8 or possibly higher is not deleterious unless prolonged.

Oxygen content of the metal varies ordinarily from 0.13 to 0.32 per cent, corresponding to 0.4 to 1.0 per cent Cr_2O_3, and may run considerably higher under certain conditions. Careful control of the cell produces metal averaging about 0.15 per cent oxygen, but efforts to eliminate the oxide have not been successful. One disadvantage of Cr_2O_3 in the chromium deposit is the fact that trees or other metal which fall off the cathodes do not dissolve completely in the catholyte. At least part of the resulting residue is fine enough to remain suspended in the bath, where it may cause pits in the deposited metal. The exact mechanism of pitting has not been de-

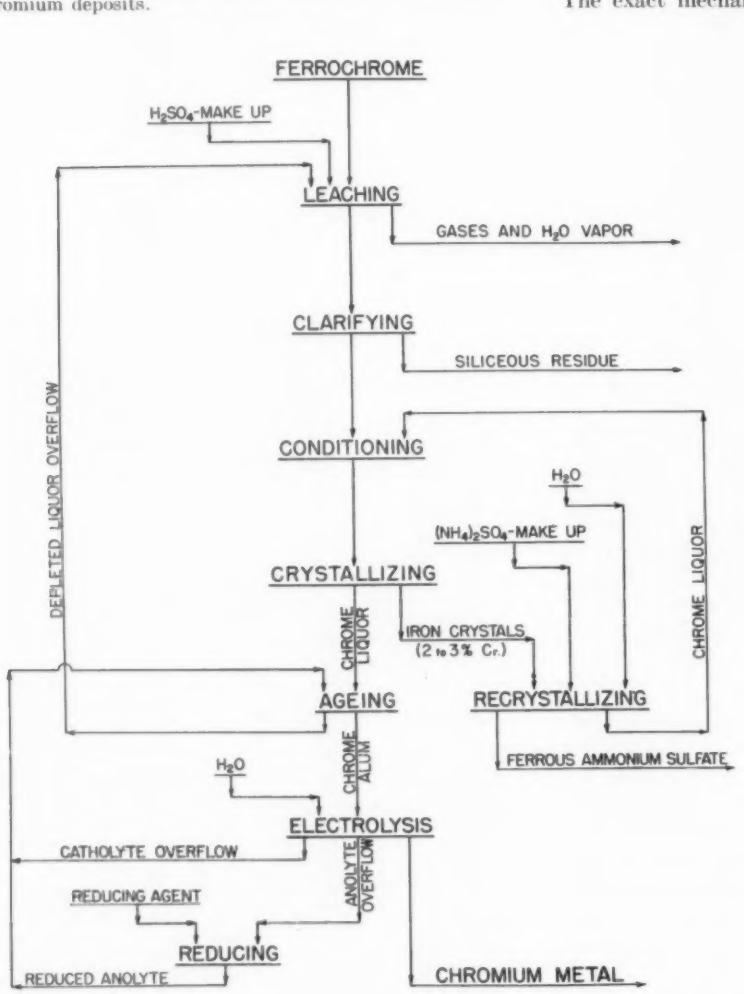

FIG. 5. Flow sheet of chromium-from-ferrochrome process.

termined, but it is believed that a suspended particle may become charged and plate out on the cathode; a funnel-shaped hole then forms with the apex on the deposited particle. This problem has been met by circulating the catholyte though a filter press, either continuously or periodically, to remove the residue. The cell may be operated for as long as ten days without filtering, and without the deposited chromium becoming noticeably pitted, but excessive pitting may start at any time. Pits tend to cause trees, which in turn fall off and cause more pits.

Oxygen in Electrolytic Chromium

All electrodeposited chromium contains oxygen (3), and the subject of the form and distribution of oxygen in chromium from the chromic acid bath has received attention by several workers. Snavely (4) gives a good review of the pertinent literature. In view of the manifest interest in the oxide occurrence, it is believed that the findings concerning oxide in chromium produced from chromium sulfate solutions would be of interest. Fig. 4, taken with a macrocamera, shows an enlarged view of two thick rough-broken, but unpolished, chromium deposits. These two samples represent opposite ends of the practical pH range; the sample on the top was deposited at the upper end of the range, and the sample on the bottom at the lower end. The high pH metal plainly shows stress cracking with dark inclusions, identified by x-ray studies as amorphous chromic oxide. Nevertheless, metal analyses consistently show less oxide in deposits of this type than in the bright, fine-textured deposits obtained at the low end of the pH range. Oxygen analyses of the samples shown were 0.15 per cent for the top sample and 0.40 per cent for the bottom sample. It will be noted that the low pH sample shows one or two striations, caused by flashing. As the number of these striations increase, the oxygen content increases. It may be concluded from the above discussion that the oxygen present in the cracks represents only part of the total oxygen.

If oxygen is attributed to the deposition of basic compounds, the upper end of the pH range would be expected to give the greatest oxide content, but the opposite is true. A precipitate caused by a high pH at the cathode surface would also be expected to contain ammonium and sulfate radicals, but no definite relationship has been noted between oxygen and either sulfate or sulfide sulfur. If the pH of the electrolyte is allowed to remain above the accepted deposition range for an extended period, basic compounds will precipitate in the solution and eventually cover the surface of the deposited metal, but this action does not appear to be the cause of the normal oxygen content of electrodeposited chromium.

Alum Preparation

Chromium ammonium alum for cell feed may be prepared directly from the ore (1), or from sodium dichromate by conventional methods, or from ferrochrome. Alum for current operations is being produced from high-carbon ferrochrome by the process flow sheet shown in Fig. 5. Detailed pilot-plant data concerning this process and the production of ferrochrome from low-grade ores will be the subject of a future publication.

Alum prepared from ferrochrome or by acid dissolution of the ore normally contains a small quantity of iron, which is deposited with the chromium, while iron-free alum is produced from sodium dichromate.

Summary

Development of a more conventional type electrolytic cell and elimination of sodium sulfate from the electrolyte has substantially decreased the cost of electrowinning chromium from chrome alum solutions. The most important economies may be listed as follows: elimination of a sodium sulfate recovery step from the cell-feed preparation flow sheet; elimination of a final aluminum-removal step from the cell-feed preparation flow sheet; a decrease in the cost of constructing the tank house by decreasing the cost per cell and increasing the production rate per cell; and a decrease in the operating labor for cell control and metal stripping. In addition to decreasing the cost of producing metal, the appearance and average purity of the chromium have been improved. Efforts to eliminate oxygen from the deposited chromium have not been successful, but some of the factors affecting oxygen content have been determined and metal containing only 0.15 per cent oxygen can be produced for extended periods.

Chromium ammonium alum suitable for cell feed has been prepared from high-carbon ferrochrome on a continuous basis.

Acknowledgments

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Any discussion of this paper will appear in a Discussion Section, to be published in the June 1951 issue of the JOURNAL.

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Gold-Plated Electrode for Measurement of Conductance of Electrolytes[1]

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ABSTRACT

Electrodes for conductance measurements by the Kohlrausch method were prepared by electrodepositing finely divided gold over a layer of smooth gold. Their behavior was studied over the frequency range 1 to 10 kilocycles/sec. Polarization resistance at these electrodes was found to be relatively small and in conformity with the Warburg relationship.

For careful measurements of the conductance of electrolytes by the Kohlrausch method (1), electrodes least subject to polarization errors are used. They are selected from those suitable for reversible hydrogen electrodes. The latter may be composed of finely divided platinum, palladium, or iridium, electrodeposited in a thin layer on one of these metals or on gold (2, 3). The choice of electrode depends upon the composition of the solution in contact with it, and various recommendations have been made, e.g., Lorch (4). The writer was faced with this choice for determining the cell constant of an electrolytic cell whose predetermined electrodes were relatively massive and of unusual shape. Machining these electrodes from precious metals was impractical; electrodeposited coatings were decided upon. Since the electrodeposition of gold in either the smooth or the finely divided state was simple and convenient, electrodes composed of finely divided gold on a gold-plated base metal were considered worthy of investigation. Miller (5) studied smooth gold-plated electrodes, using a frequency of 3,400 cycles/sec, and found definite polarization resistance. Finely divided gold surfaces, however, have not been employed previously in conductance measurements, to the writer's knowledge.

TABLE I. *Performance of the apparatus with pure resistance in place of the cell*

Frequency	R_p	C_p
cycles/sec	*ohms*	*microfarad*
1,000	19.41	0.003_5
3,000	19.41	0.003_5
5,000	19.41	0.003_5
10,000	19.41	0.003_5

TABLE II. *Conductance measurements at 25.0°C*

f	0.01*N* KCl				0.02*N* KCl			
	$R_p = R_s$	C_p	C_s	ΔR	$R_p = R_s$	C_p	C_s	ΔR
cycles/sec	*ohms*	*microfarad*	*microfarads*	*ohm*	*ohms*	*microfarad*	*microfarads*	*ohm*
1,000	43.16	0.033	410	0.13	21.99	0.105	500	0.09
2,000	43.13	0.010	340	0.10	21.96	0.033	400	0.06
4,000	43.10	0.003_3	250	0.07	21.94	0.011	300	0.04
6,000	43.08	0.001_8	210	0.05	21.93	0.006_0	240	0.03
8,000	43.08	0.001_5	140	0.05	21.93	0.004_5	180	0.03
10,000	43.08	0.001_0	140	0.05	21.93	0.003_6	150	0.03
R_T	43.03				21.90			
Λ^*	141.30				138.37			
Cell constant	0.0608_0				0.0606_1			

* Data of Shedlovsky, Brown, and MacInnes (6) increased by 0.02 per cent to correspond with the Jones and Prendergast (7) standards [see Gunning and Gordon (8)].

EXPERIMENTAL PROCEDURE AND RESULTS

The electrodeposition of gold was carried out at 60°C without agitation from the following solution:

$KAu(CN)_2$—0.050 mole/liter
KCN, free—0.20 mole/liter
K_2CO_3—0.10 mole/liter

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The cathodic current density was 0.5 amp/dm² for the adherent smooth deposit and 3.0 amp/dm² for the finely divided deposit. The cathodic current efficiency was 100 per cent at the lower current, but hydrogen was codeposited at the higher current. The electrodes, which were machined out of copper, were first plated at 0.5 amp/dm² to a thickness of 10 microns; then an additional weight of gold, equal to half that already on, was deposited in the finely divided state by raising the current.

The cell geometry, too complicated to be described in this short report, was predetermined by considerations other than conductance measurements. Very roughly, the electrodes consisted of a solid cylinder, 1.5 cm diameter, concentrically situated in a tube, 3.5 cm diameter. The conductance measurements were made by the usual Wheatstone bridge technique, employing a cathode ray oscillograph as detector and an oscillator, equipped with

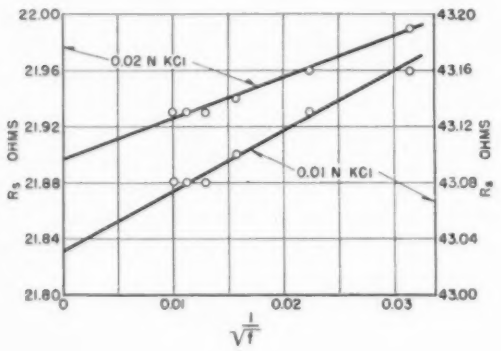

FIG. 1

an electrostatically shielded transformer at the output, as the variable frequency source. When the bridge was balanced with a pure resistance in place of the electrolytic cell, the resistance, R_p, and capacitance, C_p, in parallel with it in the adjacent arm of the bridge did not vary with frequency, f, within the limit of sensitivity of the detector (Table I).

Table II presents the conductance measurements using 0.01*N* and 0.02*N* potassium chloride solutions. R_s and C_s are the resistance and capacitance of the cell, which in series are equivalent to the parallel combination R_p and C_p. The former were computed from the measured quantities by the well-known relationships $R_s = R_p/[1 + (2\pi f R_p C_p)^2]$ and $C_s = 1/R_s R_p C_p (2\pi f)^2$. Actually the quantity $(2\pi f R_p C_p)^2$ was negligible in comparison with unity, so that $R_s = R_p$ in all cases.

Duplicate measurements of R_p at a given frequency agreed to the nearest 0.01 ohm. The true resistance of the electrolyte, R_T, was obtained using the Warburg relationship $R_s = R_T + k/\sqrt{f}$, where k is a constant. The validity of this equation has been confirmed by Jones and Christian (9) for various electrodes and electrolytes. Fig. 1 shows the data of Table II plotted according to the Warburg equation, which is in agreement with the data within experimental error.

From R_T the cell constant was calculated as $10^{-3} c\Lambda R_T$, where c and Λ are the normality and equivalent conductance of the solution, respectively. The values of the cell constant for the two solutions agree to 0.3 per cent, which is considered to be within the possible variation in the physical arrangement of this particular cell when reassembling it to change solution. For this reason, and also because the cell has an extremely low cell constant and is, therefore, unsuitable for accurate conductance measurements, the gold electrodes must be evaluated from the magnitude of the polarization resistance, $\Delta R = R_s - R_T = k/\sqrt{f}$. As seen from Table II, the polarization resistance increases to 0.3–0.4 per cent as the frequency is reduced to 1000 cycles/sec. With more favorable cells, such as those of Jones and Bollinger (10), gold electrodes plated as described herein may exhibit sufficiently less error due to polarization that no correction need be applied to the measured results for relatively accurate data. It would be of interest to determine the optimum conditions of gold plating, as Jones and Bollinger (11) did for platinization, and to compare these gold electrodes with platinized platinum electrodes in accurate conductance measurements.

Any discussion of this paper will appear in a Discussion Section, to be published in the June 1951 issue of the JOURNAL.

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Editorial

Our Society

THE ELECTROCHEMICAL SOCIETY has been undergoing some profound changes during the last three or four years. We believe that these changes are for the good of the organization and the individuals who are actively supporting it. This belief has been confirmed by favorable response from the members.

As in all democratic organizations, the changes were made in conformity with the wishes of the members, and it is gratifying to recognize that such improvements, directed toward offering more to the individual member, add to the prestige of the Society as a scientific organization. Let us examine a few of these modifications.

The constitution has been revised to make active membership available to certain people with definite qualifications. The restrictions are not stringent enough to exclude desirable individuals, but they do give professional standing to duly-elected active members. The grades of associate and student associate membership make it possible for an individual to participate in the affairs of the Society while preparing for active membership. This new membership arrangement gives a good solid foundation upon which to build a close knit group contributing to the advancement of electrochemistry.

Our publication has shown marked improvement not only in format, but in content. It is now attracting the type of papers one expects to find in a journal published by a first class professional Society.

Concurrent with the improvements in the JOURNAL is the increasing popularity of the semiannual meetings. Credit for these meetings belongs to the Divisions who have arranged fine symposia. The extensiveness of these symposia has been made possible by the new ruling that papers submitted only in abstract may be presented at the meetings.

Space does not permit a detailed list of the changes which have taken place, and a conservative might well be skeptical if confronted with the complete report. Yet the members of the Society have asked for and approved these actions, and as long as this progressive spirit continues, The Electrochemical Society will remain the leading organization in the field of electrochemistry.

HENRY B. LINFORD

THE ELECTROCHEMICAL SOCIETY, INC.

The Electrochemical Society is an international organization of individuals and companies concerned with or interested in Electrochemistry and allied subjects.

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Battery	Electro-Organic
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Electronics	

Among the means to this end are the holding of meetings for the reading and discussion of professional and scientific papers on these subjects, the publication of such papers, discussions, and communications as may seem appropriate, and cooperation with chemical, electrical, and other scientific and technical societies.

It is an incorporated society without capital stock. The affairs of the Society are managed by a Board of Directors under a Constitution and By-Laws. Officers are nominated by a nominating committee appointed by the Board of Directors and elected by the members.

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